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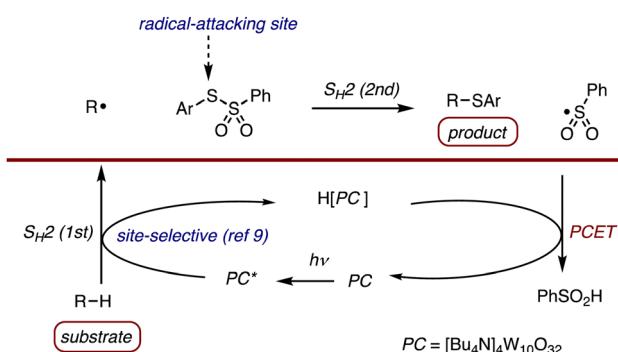
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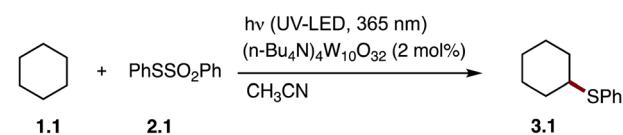
**Site-selective  $C(sp^3)$ -H thiolation using thiosulfonates has been achieved using the decatungstate anion as a photocatalyst. Using the protocol, a variety of thiolated compounds were synthesized in good yields. The transformation consists of a cascade of double  $S_{H2}$  reactions, HAT and ArS group transfer, and PCET (proton-coupled electron transfer) of the leaving arylsulfonyl radical to arylsulfonic acid thus allowing the catalyst,  $W_{10}O_{32}^{4-}$ , to be recovered.**

$C(sp^3)$ -S bonds are widely present in natural products, pharmaceuticals and value-added compounds.<sup>1</sup> Accordingly, the development of synthetic methods for C-S bond formation is highly important in organic synthesis and in chemical biology.<sup>2</sup> It is known that thiosulfonates<sup>3</sup> act as an excellent unimolecular chain transfer (UMCT) reagent<sup>4</sup> delivering an arylthio group to carbon-centred radicals in an  $S_{H2}$  (bimolecular homolytic substitution) manner resulting in the formation of thiolated compounds with liberation of arylsulfonyl radicals (Scheme 1, top equation).<sup>5</sup> Despite the broad applicability of radical thiolation reactions that involve the use of thiosulfonates, they have rarely been used for  $C(sp^3)$ -H thiolation except for a formyl C-H bond and an  $\alpha$ -C-H bond of oxygen, nitrogen and a phenyl group.<sup>6,7</sup> The use of the photocatalytic<sup>8</sup> reactions using decatungstate anion has excellent potential for use in site-selective  $C(sp^3)$ -H functionalization reaction.<sup>9</sup> The origin is the control of the  $S_{H2}$  (HAT: hydrogen atom transfer) transition states based on synergistic polar and steric effects to give the desired alkyl radicals. Combined with the excellent capability of a  $PhSO_2$  group to function as an efficient radical leaving group, recent efforts of C-H/C-C conversion include photocatalytic C-H alkenylation,<sup>10</sup> alkynylation,<sup>11,12</sup> imination,<sup>12,13</sup>

cyanation,<sup>14</sup> allylation<sup>12,15</sup> and heteroarylation.<sup>16</sup> We hypothesized that a photocatalyzed strategy using a double  $S_{H2}$  concept



**Scheme 1** Double  $S_{H2}$  strategy for site-selective  $C(sp^3)$ -H thiolation using thiosulfonates and photocatalyst.



Entry	Light <sup>b</sup>	Additive	Time (min)	Yield (%) <sup>c</sup>
1	A	none	60	47
2	A	$K_2CO_3$	60	78
3	A	$K_2CO_3$	30	64
4	B	none	60	38
5 <sup>d</sup>	B	none	60	0
6	B	none	480	65
7	C	$K_2CO_3$	960	22

<sup>a</sup>General conditions: Pyrex test-tube, **1.1** (2.5 mmol), **2.1** (0.5 mmol),  $(n-Bu_4N)_4W_{10}O_{32}$  (0.01 mmol), additive (none or 0.5 mmol), acetonitrile (1 mL), photoirradiation (365 nm). <sup>b</sup>A, high power UV-LED (365 nm, 480 W, MiChS UV-LED-s); B, low power UV-LED (365 nm, 3.4 W, PENN PhD Photoreactor M2 from Sigma-Aldrich); C, blacklight (365 nm, 15 W, Toshiba Inc.). <sup>c</sup> Isolated yields after silica gel chromatography. <sup>d</sup>Without catalyst.

**Scheme 2** Photocatalytic C-H phenylthiolation of cyclohexane **1.1** using S-phenyl benzenethiosulfonate **2.1**.

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(HAT plus  $S_{H2}$  at sulfur atom) using phenylthiobenzenesulfonate as a thiolating reagent and decatungstate anion as a catalyst would be promising (Scheme 1) for allowing for site-selective C–H thiolation to be achieved.

To establish optimal conditions for this reaction, we initially surveyed a photocatalytic C–H thiolation using cyclohexane **1.1** and  $\text{PhSSO}_2\text{Ph}$  **2.1** in the presence of 2 mol% of decatungstate anion as a model reaction (Scheme 2). For a light source we examined a power-adjustable high-power LED (365 nm, 480 W, MiChS-UV-LED-s)<sup>17</sup> and a low-power LED (365 nm, 3.4 W (PENN PhD Photoreactor M2, Sigma-Aldrich). The former gave a 47% yield of the desired phenylthiolated cyclohexane **3.1** after photoirradiation for 1 h (entry 1), while the latter gave 38% after 1 h (entry 4) and 65% after 8 h (entry 6). Photoirradiation without catalyst did not give **3.1** (entry 5). The addition of

$\text{K}_2\text{CO}_3$  as a base increased the yield of **3.1** to 78% yield (entry 2). A shorter reaction time of 30 min caused the yield to be decreased to 64% (entry 3). We also tested blacklight irradiation (15 W, 16 h) but was not so effective (entry 6).

On the basis of the protocol of entry 2, we then investigated the scope and limitations of the photocatalytic  $\text{C}(\text{sp}^3)\text{–H}$  thiolation for a wide range of organic compounds, the results for which are summarized in Table 1. The thiolation of cyclic alkanes such as cyclohexane, cyclopentane, cycloheptane, cyclooctane and cyclododecane gave thioethers **3.1** (78%), **3.2** (58%), **3.3** (61%), **3.4** (54%) and **3.5** (27%), respectively. The use of *p*-chlorotoluene gave the corresponding benzyl thioether **3.6** in 42% yield. The thiolation of linear ethers such as diethyl ether, *t*-butyl methyl ether, ethyl phenolate, anisole, and *p*-chloroanisole afforded the corresponding thioethers **3.7**

Table 1 Photocatalytic  $\text{C}(\text{sp}^3)\text{–H}$  thiolation of **1** by thiosulfones **2<sup>a</sup>**

$\text{R}=\text{H}$	$\text{ArSSO}_2\text{Ph}$	$(\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ (2 mol%)	$\text{R}=\text{SPh}$
<b>1</b> 2.5 mmol	<b>2</b> 0.5 mmol	$\text{K}_2\text{CO}_3$ (0.5 mmol), MeCN 365 nm, 480 W, 1 h	<b>3</b>
<b>3.1</b> 78%			<b>3.2</b> 58% <sup>b,c</sup>
<b>3.3</b> 61%			
<b>3.4</b> 54%			
<b>3.5</b> 27%			
<b>3.6</b> 42%			
<b>3.7</b> 69%			
<b>3.8</b> 38%			
<b>3.9</b> 35%			
<b>3.10</b> 42%			
<b>3.11</b> 36%			
<b>3.12</b> 41% (90/10)			
<b>3.13</b> 34%			
<b>3.14</b> 83%			
<b>3.15</b> 67%			
<b>3.16</b> 67%			
		$\text{Ar} = \text{C}_6\text{H}_4\text{–}p\text{-Me}$	
<b>3.17</b> 85%			
		$\text{C}_6\text{H}_4\text{–}p\text{-Cl}$	
<b>3.18</b> 78%			
		$\text{C}_6\text{H}_4\text{–}p\text{-Br}$	
<b>3.19</b> 64%			
<b>3.20</b> 59%			
<b>3.21</b> 63%			
<b>3.22</b> 71%			
<b>3.23</b> 44%			
<b>3.24</b> + <b>3.24'</b> 72% (59/41)			
<b>3.25</b> 61%			
<b>3.26</b> + <b>3.26'</b> 39% (67/33)			
<b>3.27</b> 50% (96/4)			
<b>3.28</b> 43%			
<b>3.29</b> 64% <sup>b,c</sup>			
<b>3.30</b> 50% (94/6)			
<b>3.31</b> 80%			
<b>3.32</b> 62% <sup>b,c</sup>			
<b>3.33</b> 31%			

<sup>a</sup> General conditions: **1** (2.5 mmol), **2** (0.5 mmol),  $(\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$  (0.01 mmol),  $\text{K}_2\text{CO}_3$  (0.5 mmol), acetonitrile (1 mL), photoirradiation using UV-LED (365 nm, 480 W) under  $\text{N}_2$  atmosphere for 1 h. Isolated yields after silica gel column chromatography are given. The ratios were determined by  $^1\text{H}$  NMR. <sup>b</sup> UV-LED (365 nm, 360 W). <sup>c</sup> 1.5 h. <sup>d</sup>  $(\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ : 4 mol%.

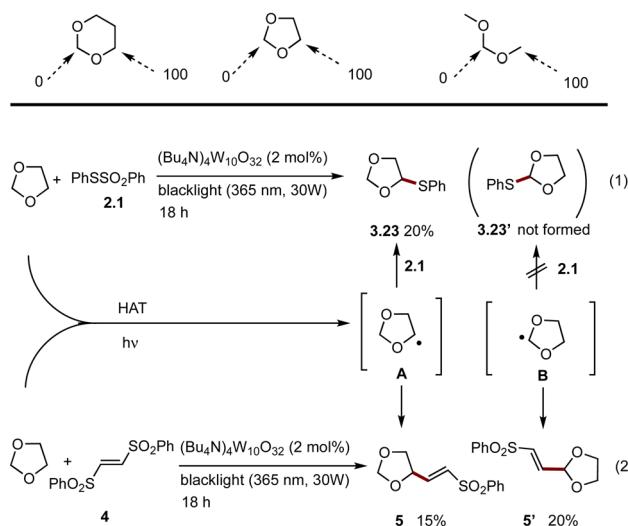


(69%), **3.8** (38%), **3.9** (35%), **3.10** (42%) and **3.11** (36%). In the reaction of *p*-methylanisole, the ether  $\alpha$ -C–H reacted preferentially compared to the  $\alpha$ -benzylic C–H, giving **3.12** as a major product (90/10) in a total yield of 41%. Thioanisole was converted into the dithioacetal **3.13** albeit the modest yield. The reaction of cyclic ethers such as THF, tetrahydropyran and 1,4-dioxane proceeded smoothly to give **3.14** (83%), **3.15** (67%) and **3.16** (67%), respectively. Three different arylthio groups were confirmed to be introduced into 1,4-dioxane using  $\text{ArS-SO}_2\text{Ph}$  ( $\text{Ar} = p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4$ ), giving **3.17** (85%), **3.18** (78%) and **3.19** (64%), respectively. Using a similar photocatalytic protocol, the use of *n*-Bus-SO<sub>2</sub>Ph produced the corresponding butyl sulfide **3.20** in 59% yield. The reaction of 1,3-dioxane gave **3.21** (63%) selectively which was derived from H-abstraction at the 4-position rather than the 2-position. The reaction of 2,2-dimethyl-1,3-dioxolane and 1,3-dioxolane with **2.1** gave **3.22** (71%) and **3.23** (44%), respectively. The reaction of dimethoxyethane gave a 59/41 mixture of **3.24** and **3.24'** *via* methylene and methyl C–H bond cleavage in a 72% total yield. The reaction of dimethoxymethane took place selectively at the methyl-C–H bond to give **3.25** as a sole product in 61% yield.

We then examined the thiolation of cyclic ketones and lactones. The reaction of cyclohexanone gave a 67/33 mixture of **3.26** and **3.26'** in 39% yield. In 4-methylcyclohexanone, methine C–H thiolation occurred selectively, giving **3.27** (96/4) in 50% yield. The thiolation of 3,3-dimethylcyclohexanone was site-selective at the 5-methylene to give **3.28** in 43% yield. The thiolation of cyclopentanone gave **3.29** as the sole product in 64% yield. The thiolation of  $\gamma$ -butyrolactone proceeded highly selectively at the methylene bond  $\alpha$  to the oxygen (94/6), giving **3.30** in 50% yield. The thiolation of  $\gamma$ -valerolactone took place at the methine C–H to give **3.31** as the sole product in 80% yield. The thiolation of *N*-acetyl piperidine and *N*-trifluoroacetyl piperidine proceeded site-selectively to give the thiolation products **3.32** (62%) and **3.33** (31%), respectively. The thiolation of *N*-acetyl morpholine proceeded exclusively at the *N*-methylene group, giving the corresponding thioether **3.34** in 47% yield. The thiolation of *N,N*-dimethylacetamide took place selectively at the *N*-methyl group to give **3.35** in 83% yield. The thiolation of *N*-methyl-2-pyrrolidinone occurred highly selectively at the  $\alpha$ -methylene C–H bond to the  $\alpha$ -methyl C–H bond, to give **3.36** as the major product (91/9) in 65% total yield. The thiolation of *N,N*-dimethylformamide (DMF) gave the methyl-thiolation product **3.37** in 42% yield. This is in contrast with the reaction of DMF with thiosulfonate using Rhodamine B as a photocatalyst, giving thiocarbamate *via* the generation of a carbamoyl radical.<sup>18,19</sup> The scalability of the present protocol was confirmed by the reaction of **1.1** using 5 mmol of **2.1**, which gave 71% (685 mg) yield of **3.1** (see ESI<sup>†</sup>).

Concerning the 1,3-dioxolanes, **3.21**, **3.23** and **3.25**, interestingly, the thiolation products at  $\alpha$ -C–H bonds that were activated only by a single oxygen atom were obtained selectively. To avoid a possibility of the degradation of products we used milder irradiation (blacklight, 30 W) for the reaction of 1,3-dioxolane with **2.1** (Scheme 3, eqn (1)). As our expectation, the reaction was sluggish and after 18 h it gave 20% yield of **3.23**

### Thiolation selectivity for **3.21**, **3.23** and **3.25**

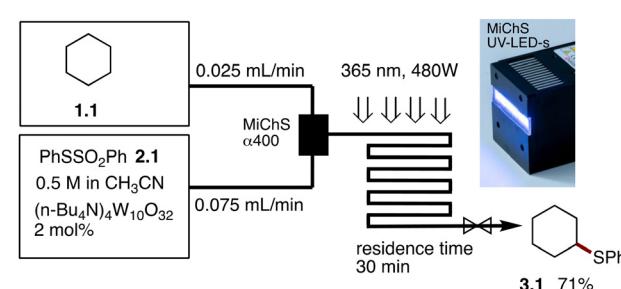


Scheme 3 Comparison of  $\text{C}(\text{sp}^3)\text{-H}$  thiolation and alkenylation for 1,3-dioxolane.

as only thiolated product together with a large amount of **2.1** remained unreacted. Using similar photoirradiation conditions, we carried out decatungstate-catalyzed alkenylation of 1,3-dioxolane using **4**,<sup>10</sup> which gave a mixture of alkenylated products **5** and **5'** (Scheme 3, eqn (2)), suggesting the first  $\text{S}_{\text{H}2}$  takes place at both C–H bonds to generate radical **A** and **B**. Accordingly, we concluded that the second  $\text{S}_{\text{H}2}$  with thiosulfone **2.1** is inefficient for radical **B** stabilized by two adjacent oxygens, rendering the site-selective  $\text{C}(\text{sp}^3)\text{-H}$  thiolation to give **3.23**.<sup>20</sup>

Finally, we examined the flow photocatalytic reaction (Scheme 4),<sup>21</sup> using a flow setup consisting of a tubular PFA reactor (inner diameter = 1 mm, outer diameter = 1.56 mm, length = 3.82 m, total inner volume = 3 mL) and high-power LED (365 nm, 480 W, MiChS UV-LED-s). An acetonitrile solution containing **2.1** (500 mM) and the decatungstate anion (2 mol%) was mixed with neat cyclohexane **1.1** using a T-shaped mixer with a 400  $\mu\text{m}$  inner diameter (MiChS  $\alpha$ 400) and introduced into a photo flow reactor connected with a back pressure regulator (5 psi). Irradiation with a residence time of 30 min resulted in the formation of the envisaged cyclohexyl phenyl sulfide **3.1** in 71% isolated yield.

In summary, we have reported herein on a photocatalytic protocol for the thiolation of  $\text{C}(\text{sp}^3)\text{-H}$  bonds using



Scheme 4 Flow photocatalytic thiolation.



thiosulfonates **2**. The decatungstate anion functions as an excellent photocatalyst for introducing sulfur-functions to organic molecules **1**. The site-selective thiolation protocol is applicable to a wide range of functionalized aliphatic compounds, such as ethers, ketones, esters, ethers and amides, thus greatly expanding the utility of radical-based C(sp<sup>3</sup>)-H thiolation chemistry.

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## Conflicts of interest

There are no conflicts to declare.

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